

Computational Investigation on Electronic Structures and Properties of 4,6-bis(nitroimino)-1,3,5-triazinan-2-one: An Insensitive Munition Compound

Katarina M. Pittman,^{†,‡} Harley R. McAlexander,[†] Gregory S. Tschumper,[‡] and
Manoj K. Shukla^{*,†}

[†]*US Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg,
MS 39180*

[‡]*Department of Chemistry and Biochemistry, University of Mississippi, University, MS
38677-1848*

E-mail: Manoj.K.Shukla@usace.army.mil

Phone: 601-634-5431

Abstract

In order to minimize unintentional detonation munitions researchers have focused on the development of chemical compounds that are insensitive to external stimuli while maintaining their effectiveness. While these compounds, known as high performance insensitive munitions compounds, are promising in terms of potency and stability, their environmental impacts have either not been fully understood or are yet to be investigated. In the present research, we have performed a quantum chemical investigation on electronic structures and properties of an insensitive munition compound 4,6-bis(nitroimino)-1,3,5-triazinan-2-one (DNAM). The density functional theory using the B3LYP and M06-2X functionals and MP2 methodology were used for geometry optimization of various tautomeric forms of DNAM. The effect of bulk water solution was evaluated using the conductor-like polarizable continuum model (CPCM) and the density-based solvation model (SMD). Ionization potential, electron affinity, redox properties, and pK_a values were also computed and were compared with the available experimental data. These physical and chemical properties of DNAM have been discussed in regard to the varying tautomeric forms in which DNAN can exist.

Keywords: DNAM, reduction potential, oxidation potential, ionization potential, electron affinity

Introduction

While legacy high energy density materials such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) serve as effective munitions compounds, they can have a relatively high risk of unintentional detonation during manufacturing, handling, transportation, and storage due to their sensitivity to external stimuli.¹ Consequently, there is an increased interest in the development of high energy density materials that are not only insensitive to external stimuli, but also maintain effectiveness while minimizing their environmental impact.¹⁻⁵ These materials, dubbed insensitive munitions, demonstrate high thermal stability and low impact sensitivity to friction and electrostatic discharge.^{6,7}

Certain heterocyclic nitrogen-containing compounds form highly energetic salts that are both effective munitions candidates yet environmentally safe due to the high percentage of dinitrogen in their decomposition products.⁸ Furthermore, they have the advantage of high positive heats of formation rather than heats of combustion as in the case of traditional munitions.⁹ One promising material is 4,6-bis(nitroimino)-1,3,5-triazinan-2-one (also known as 4,6-dinitramino-1,3,5-triazine-2(1H)-one, dinitroammeline, or simply DNAM). First synthesized in 1951, this compound has been shown to exhibit the aforementioned characteristics desired in insensitive munitions.¹⁰⁻¹⁶

Although DNAM has been the subject of several theoretical studies, only a limited number of efforts have focused specifically on the most stable conformers. Simões *et al.*¹⁷ conducted a joint experimental and theoretical investigation on DNAM using MP2 and density functional theory (DFT) methods and showed the presence of different tautomers. They found that, in the gas phase, tautomers possessing nitroimine groups are more stable than those with nitramine groups. Of these tautomers, the so-called NIC (nitro, imine, keto) series was identified as the most probable of the nitroimine forms, with its third conformer found to exist in the crystalline structure of DNAM.¹⁷ Gao *et al.*⁷ examined the thermal stabilities of several energetic salts using the Born-Haber energy cycle to determine heats of formation. In addition to the triazole salts being thermally stable, the detonation velocities and pressures were comparable to those of common explosives and even exceeded those of TNT. DNAM salts also exhibited large positive heats of formation.⁷ Limited

investigation has been conducted regarding the acidity of DNAM; in 2001, Simões *et al.* (2001),¹⁴ using potentiometric titration and the Henderson-Hasselbalch equation, has measured the pK_a of DNAM to be 3.2, showing the acidic nature of this compound.

Through advanced quantum chemical calculation and using relative energies, adiabatic electron affinities and ionization potentials, and reduction/oxidation (redox) potentials, this manuscript highlights the differences between the three conformers of the most stable tautomer and examines the manner in which DNAM responds to an aqueous environment by exploring potential reactivity. The pK_a 's are also computed for further determination of the degree of ionization and propensity for sorption to soil and sediment, which is highly significant in determining environmental fate of munitions compounds.¹⁸

Computational Details

In this study, we optimized geometries using two quantum chemical methods based on density functional theory (DFT) as well as second-order Møller-Plesset perturbation theory (MP2).^{19–22} All calculations were performed with the Pople-style split valence 6-311++G(d,p) basis set. The DFT calculations utilized both the Becke-style 3-parameter exchange functional combined with the Lee-Yang-Parr correlation functional (B3LYP) and the Minnesota 06 hybrid functional (M06-2X) as implemented in Gaussian16 for comparison.²³ B3LYP is one of the most widely used functionals, and M06-2X has shown good accuracy for thermodynamic property calculations in solution.^{24–26} Harmonic vibrational frequencies were calculated using the same methods and basis set to ascertain the nature of potential energy surfaces. The absence of imaginary frequencies confirms that the computed conformers are at a minimum on their respective potential energy surfaces. In order to consider structural changes in solution, geometry optimizations and corresponding harmonic vibrational frequency calculations were additionally performed using two implicit solvent approaches — the conductor-like polarizable continuum model (CPCM)²⁷ and the density-based solvent model (SMD)²⁸ — with the default solvent parameters for water available

in Gaussian16. For the computation of environmentally relevant physical properties of DNAM (Table 5), we employed TURBOMOLE²⁹ to generate COSMO files that were in turn used in the COSMOthermX^{30–33} program.

In previous studies concerning DNAM, four tautomeric forms have been identified — NAC, NAE, NIC, and NIE (with the NIC series identified as the most stable tautomer by ≈ 30 kcal mol⁻¹).¹⁷ These tautomers are distinguished by the presence of keto versus enol (“C” vs “E”) and nitroimine versus nitramine (“NI” vs “NA”) moieties, as can be seen in Figure 1 where examples of each tautomer are depicted. In this study, we focused on the NIC series, which possesses the

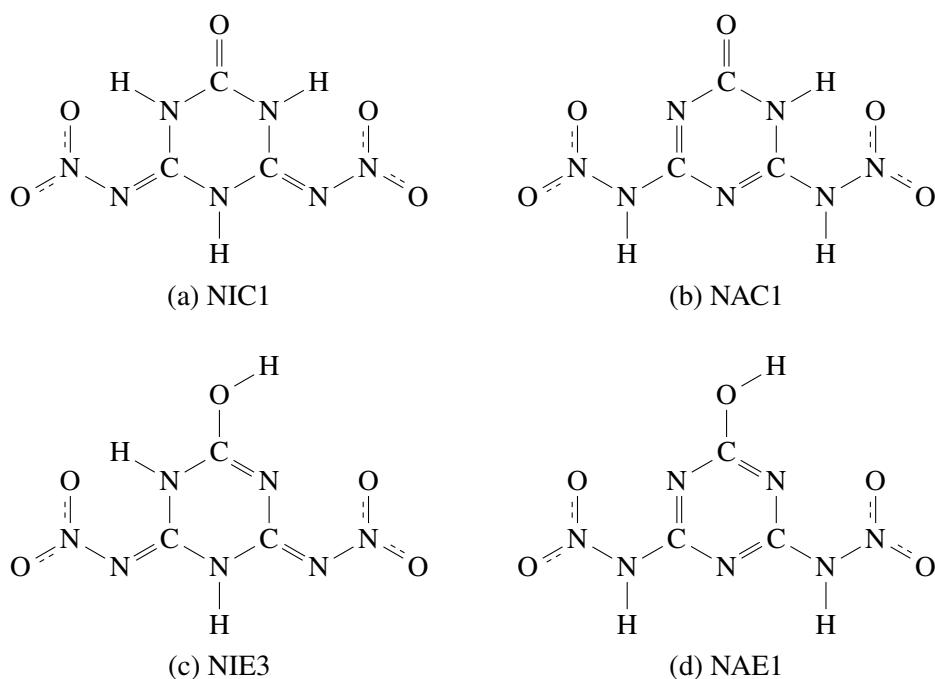


Figure 1: One conformer from each of the tautomer groups (NIC, NAC, NIE, and NAE).

keto and nitroimine moieties and has three conformers depending upon the orientation of the nitro groups (i.e., NIC1, NIC2, and NIC3), which are displayed in Figure 2. The MP2 geometries exhibit very slight non-planarity at the nitro groups, which may rotate in a parallel or anti-parallel fashion relative to one another depending on the starting structure. The energy difference between the two was well within thermal fluctuations (0.529 kcal/mol), and we selected the lowest energy conformer in each case.

Vertical electron affinities (VEA) and ionization potentials (VIP) were calculated by taking the

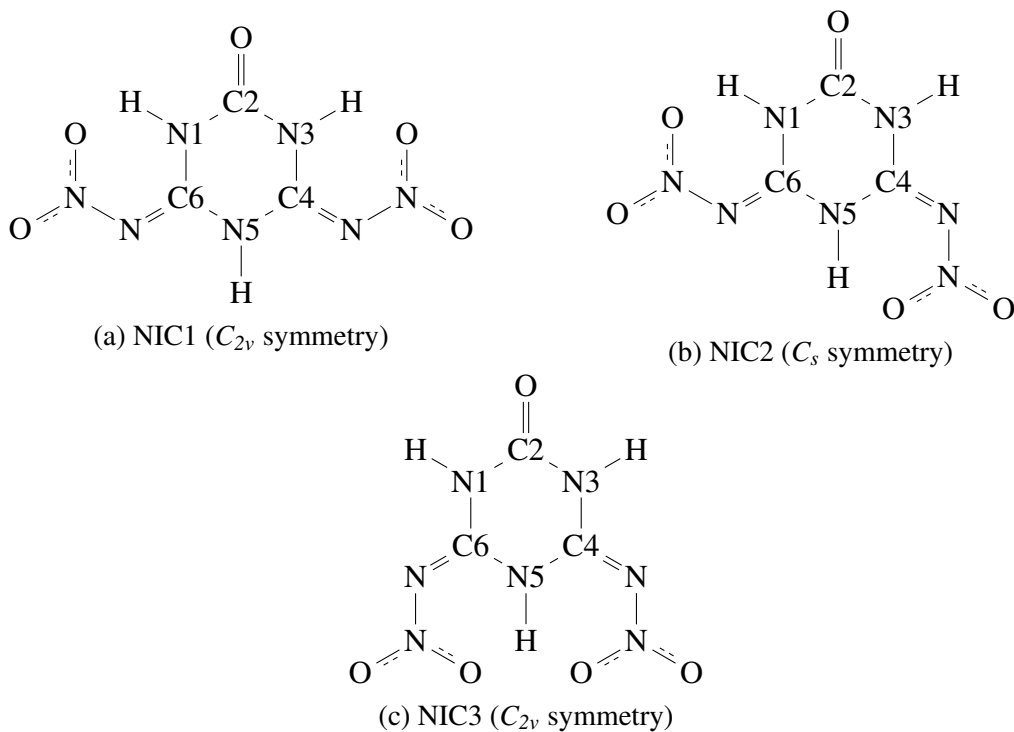


Figure 2: The three conformers in the NIC series of DNAM.

difference between the total energy of the fully optimized ground state of DNAM and the one-electron reduced or oxidized forms at the optimized ground state reference geometry as shown in Equations 1 and 2,

$$\text{VEA} = -(E^{\bullet-} - E) \quad (1)$$

$$\text{VIP} = E^{\bullet+} - E \quad (2)$$

where E represents the total energy of DNAM, and $E^{\bullet+}$ and $E^{\bullet-}$ represent the total energy of the radical cation and radical anion forms, respectively, of DNAM at the ground state reference geometry.

For the adiabatic EA and IP values, the corresponding radical anionic and cationic species are

also fully optimized:³⁴

$$\text{AEA} = -(E_{\text{opt}}^{\bullet-} - E) \quad (3)$$

$$\text{AIP} = E_{\text{opt}}^{\bullet+} - E \quad (4)$$

where $E_{\text{opt}}^{\bullet+}$ and $E_{\text{opt}}^{\bullet-}$ represent the energies of the separately optimized radical cation and anion forms of DNAM, respectively.

For the reduction potentials in both the gas phase and in water solution, we employed the Nernst equation,

$$E_{\text{red}}^{\circ} = -\frac{\Delta G_{\text{red}}^{\circ}}{nF} + E_{\text{H}} \quad (5)$$

$$E_{\text{ox}}^{\circ} = \frac{\Delta G_{\text{ox}}^{\circ}}{nF} + E_{\text{H}} \quad (6)$$

where E_{red}° and E_{ox}° are the reduction and oxidation potentials, respectively, in either the gas phase or in water solution; n is the number of electrons ($n=1$); F is the Faraday constant (96,485.3 C mol⁻¹); and E_{H} is the potential for the standard hydrogen electrode (-4.28 eV).³⁵⁻³⁹ $\Delta G_{\text{red}}^{\circ}$ is the Gibbs free energy required to attach adiabatically an electron to the DNAM conformer in either the gas phase or in water solution, and likewise $\Delta G_{\text{ox}}^{\circ}$ is the Gibbs free energy necessary to remove an electron adiabatically in the gas phase or in water solution. These terms may be interpreted as simple differences in Gibbs free energy between the radical and neutral species, as shown in Eqs 7-8,

$$\Delta G_{\text{red}}^{\circ} = G_{\text{opt}}^{\bullet-} - G \quad (7)$$

$$\Delta G_{\text{ox}}^{\circ} = G_{\text{opt}}^{\bullet+} - G \quad (8)$$

where G is the Gibbs free energy of neutral DNAM, and $G_{\text{opt}}^{\bullet+}$ and $G_{\text{opt}}^{\bullet-}$ are the Gibbs free energies of the radical cation and anion forms of DNAM, respectively.

In calculating the $\text{p}K_{\text{a}}$ s, we considered the single deprotonation of DNAM. The resulting an-

ionic form of DNAM was accomplished by deprotonating one of the three nitrogens in the central triazine ring. NIC1 and NIC3 were only deprotonated at two nitrogens (N1 and N5), due to the symmetric nature of the nitro groups, while all three nitrogens in NIC2 were deprotonated (N1, N3, and N5). The labeling of the ring nitrogens are shown in Figure 2. For the pK_a calculations, we used the following equation,

$$pK_a = \frac{\Delta G_{\text{solv}}}{RT \ln 10} \quad (9)$$

where R is the gas constant in $\text{kcal mol}^{-1} \text{K}^{-1}$, T is the temperature of the system (298.15 K), and ΔG_{solv} is the deprotonation energy of DNAM in water. The ΔG_{solv} was computed by using Eq 10,

$$\Delta G_{\text{solv}} = G_{\text{solv}}(\text{H}^+) + G_{\text{solv}}(\text{DNAM}^-) - G_{\text{solv}}(\text{DNAM}), \quad (10)$$

where $G_{\text{solv}}(\text{DNAM}^-)$ and $G_{\text{solv}}(\text{DNAM})$ represent the Gibbs free energy of the deprotonated and neutral forms of DNAM, respectively, in the bulk water solution. The $G_{\text{solv}}(\text{H}^+)$ was computed by using Eq 11,

$$G_{\text{solv}}(\text{H}^+) = \Delta G_{\text{solv}}(\text{H}^+) + G_{\text{gas}}(\text{H}^+). \quad (11)$$

The term involving H^+ presents a challenge and can give rise to large errors in pK_a calculations. Thus, we have applied an experimental value of $\Delta G_{\text{solv}}(\text{H}^+)$, $-265.9 \text{ kcal mol}^{-1}$ at 1 M concentration as recommended by Alongi and Shields (which includes the correction of Ben-Naim and Marcus⁴⁰ for changes in standard state from 1 atm to 1 M),¹⁸ while $G_{\text{gas}}(\text{H}^+)$ has been determined experimentally and is widely accepted as $-6.28 \text{ kcal mol}^{-1}$ at 1 atm.^{18,41-45} From these two values, we can calculate the free energy of the H^+ in solution using Eq 11, which amounts to $272.18 \text{ kcal mol}^{-1}$. However, we need to adjust for the difference in standard states (1 atm vs 1 M) for the

two values via the correction factor below:

$$\Delta G^{\circ \rightarrow *}=RT\ln(24.4564) \tag{12}$$

yielding 1.89 kcal mol⁻¹ at a temperature of 298.15 K. With this adjustment, we arrive at our final value of -270.28 kcal mol⁻¹ at 1 atm for the free energy of H⁺ in solution.

Results and Discussion

Table 1 collects the Boltzmann percentage distributions (p_i) for each NIC conformer of DNAM, while relative electronic and Gibbs free energies are shown in Table S1-S2 of the Supporting Information. Each distribution was calculated using Eq 13, where ΔG_i is the relative Gibbs free energy of NIC conformer i , R is the gas constant, and T is temperature (298.15 K).

$$p_i = \frac{e^{-\Delta G_i/RT}}{\sum_{j=1}^M e^{-\Delta G_j/RT}} \tag{13}$$

In the gas phase, the DFT results agree that NIC3 will have a marginal contribution, while MP2, on the other hand, predicts that NIC3 will contribute nearly as much as NIC1 at 298.15 K. Moreover, M06-2X and MP2 predict that the population of NIC2 will be more than NIC1 in the gas phase. With the inclusion of bulk water effects, the NIC3 conformer population was found to increase as predicted by all three methods. With the SMD model, B3LYP favors the NIC1 conformer, M06-2X essentially equally weights all three, while MP2 has a major shift towards the NIC1 conformer but shows even treatment between NIC1 and NIC3. It appears that all three conformers would be present in the water solution.

Computed EA's and IP's, displayed in Table 2, reveal similar trends in the gas phase and bulk water solution. MP2 tends to predict electron affinities less than the DFT methods by around 1 eV, but the ionization potentials are generally in much better agreement, especially for the adiabatic

Table 1: Boltzmann distributions for the NIC conformers of DNAM using B3LYP, M06-2X, and MP2 levels and the 6-311++G(d,p) basis set.

Solvation Model [†]	Conformer	B3LYP	M06-2X	MP2
None	NIC1	0.58	0.39	0.18
	NIC2	0.40	0.57	0.66
	NIC3	0.02	0.04	0.16
CPCM	NIC1	0.35	0.24	0.27
	NIC2	0.36	0.22	0.35
	NIC3	0.29	0.54	0.37
SMD	NIC1	0.61	0.33	0.41
	NIC2	0.22	0.36	0.20
	NIC3	0.17	0.31	0.39

[†]Solvation model ‘None’ represents gas phase results.

values. In a study by Cooper et al.,⁴⁶ a similar trend was reported for the difference in density functional and MP2 ionization potentials and electron affinities, which is also reflected in the redox properties. When the implicit solvent models are applied, the EA’s increase while the IP’s decrease. This trend is evident for each method and should be attributed to the stabilization of ionic species in the bulk water solution. The overall shifts with respect to phase suggest that when in water, DNAM will exhibit higher reactivity.

Table 2: Vertical and adiabatic electron affinities (EA) and ionization potentials (IP) using B3LYP, M06-2X, and MP2 with the 6-311++G(d,p) basis set. All values are shown in eV.

Solvation Model	Conformer	B3LYP				M06-2X				MP2			
		VEA	AEA	VIP	AIP	VEA	AEA	VIP	AIP	VEA	AEA	VIP	AIP
None	NIC1	2.1	2.4	10.4	10.1	1.8	2.1	11.0	10.6	1.0	1.2	11.3	10.3
	NIC2	2.1	2.4	10.4	10.2	1.8	2.2	11.1	10.6	1.1	1.3	11.5	10.3
	NIC3	2.0	2.3	10.3	10.1	1.7	2.1	11.4	10.6	0.8	1.2	14.1	10.3
CPCM	NIC1	3.6	3.8	8.3	8.0	3.1	3.7	9.0	8.4	2.4	2.6	9.0	8.0
	NIC2	3.7	3.9	8.3	8.0	3.1	3.7	9.0	8.4	2.5	2.8	9.0	8.0
	NIC3	3.7	3.9	8.7	8.0	3.4	3.7	9.2	9.0	2.4	2.8	9.0	8.0
SMD	NIC1	3.7	3.9	8.1	7.7	3.2	3.8	8.7	8.1	2.2	2.6	8.7	7.6
	NIC2	3.7	3.9	8.1	7.8	3.3	3.9	8.8	8.1	2.3	2.7	8.8	7.7
	NIC3	3.8	4.0	8.5	7.8	3.3	3.9	8.9	8.8	2.4	3.4	8.7	7.7

The oxidation and reduction potentials of all three conformers of DNAM in water solution are shown in Table 3. For educational curiosity, the corresponding values in the gas phase are shown in the SI. For the reduction potentials, more positive values indicate a higher likelihood of reduction, while the reverse is true for oxidation potentials. It is clear from Table 3 that both DFT functionals agree with respect to the prediction of redox potentials. The oxidation potentials at the MP2 level are generally in good agreement with those predicted using the DFT functionals, but MP2 predicted relatively lower reduction potentials. Moreover, both the CPCM and SMD predictions are in excellent agreement and all three conformers have similar corresponding values.

Table 3: Reduction (E_{red}°) and oxidation (E_{ox}°) potentials using B3LYP and M06-2X with the 6-311++G(d,p) basis set. All values are shown in eV.

Solvation Model	Conformer	B3LYP		M06-2X		MP2	
		E_{red}°	E_{ox}°	E_{red}°	E_{ox}°	E_{red}°	E_{ox}°
CPCM	NIC1	-0.5	3.7	-0.6	4.1	-1.7	3.6
	NIC2	-0.4	3.7	-0.5	4.0	-1.4	3.7
	NIC3	-0.4	3.7	-0.5	4.8	-1.6	3.6
SMD	NIC1	-0.4	3.5	-0.4	3.8	-1.9	3.3
	NIC2	-0.3	3.5	-0.4	3.8	-2.1	3.4
	NIC3	-0.4	3.5	-0.4	4.4	-0.9	3.4

The presence of the nitroimino groups on the NIC series (see Figure 2) likely causes a significant electron-withdrawing effect on the ring structure, and this could promote acidic behavior for DNAM. This is apparent in the pK_a results shown in Table 4, where the majority of pK_a values range from around -3 to 1 (relatively strong acid to weak acid). MP2 often predicts pK_a values between B3LYP and M06-2X, while M06-2X tends to yield the most acidic pK_a s; for example, the N5 nitrogen of NIC1/M06-2X/SMD has a pK_a of -4.5 compared to -1.8 for MP2/SMD. Nonetheless, the N5 nitrogen is generally the most acidic for all methods, with B3LYP/CPCM for NIC3 and B3LYP/SMD for NIC3 being the notable exceptions; and the N1 site is predicted to be the least acidic (with few exceptions: B3LYP/SMD,CPCM for NIC3).

Moreover, several environmentally relevant parameters were computed using the COSMOth-

Table 4: Predicted pK_a values using B3LYP, M06-2X, and MP2 levels and the 6-311++G(d,p) basis set.

Conformer	Nitrogen	CPCM			SMD		
		B3LYP	M06-2X	MP2	B3LYP	M06-2X	MP2
NIC1	N1	1.1	-1.7	-0.6	0.6	-0.9	0.5
	N5	-3.3	-4.6	-1.9	-2.9	-4.5	-1.8
NIC2	N1	1.0	-1.4	-0.2	1.3	-1.6	-0.1
	N3	-0.7	-2.7	0.1	-0.3	-2.8	0.0
	N5	-1.5	-3.9	-2.3	-1.1	-3.6	-1.8
NIC3	N1	-0.4	-2.1	0.4	-1.6	-2.6	0.1
	N5	-0.1	-3.2	-3.0	-0.3	-2.8	-2.6

ermX program.^{30–33} This program uses screening densities (σ -profile) from quantum chemistry calculations, and computed properties are shown in Table 5.

Table 5: Physical properties computed using COSMOthermX at the BP86/TZVP level using the B3LYP, M06-2X, and MP2 geometries with the 6-311++G(d,p) basis set.

Method	Conformer	VapPress[Pa]	K_H [C_g/C_{aq}]	w_{solub} [g/L]	Log K_{ow}	Log $K_{\text{hept-w}}$	Log K_{oc}	T_{boil} [C]	T_{flash} [K]
B3LYP	NIC1	1.02×10^{-4}	8.24×10^{-10}	10.9	0.34	-2.25	1.84	527	553
	NIC2	1.03×10^{-4}	8.58×10^{-10}	10.6	0.34	-2.23	1.82	528	554
	NIC3	4.02×10^{-5}	9.77×10^{-11}	35.5	0.09	-3.30	1.85	542	565
M06-2X	NIC1	1.30×10^{-4}	9.55×10^{-10}	12.0	0.29	-2.28	1.80	520	550
	NIC2	1.20×10^{-4}	9.13×10^{-10}	11.6	0.30	-2.26	1.79	523	551
	NIC3	6.26×10^{-5}	1.53×10^{-10}	35.2	0.11	-3.23	1.84	531	559
MP2	NIC1	2.67×10^{-4}	2.42×10^{-9}	9.7	0.62	-1.96	1.98	505	539
	NIC2	2.56×10^{-4}	2.12×10^{-9}	10.6	0.54	-2.07	1.93	504	539
	NIC3	2.23×10^{-4}	6.96×10^{-10}	27.8	0.52	-2.75	2.08	504	540

The Henry's law constants are all quite small (on the order of 10^{-9} - 10^{-10}), which agrees with the predicted low magnitude vapor pressures, suggesting that DNAM will not volatilize readily. While the solid is stable, DNAM is predicted to be highly soluble in water with the NIC3 conformer usually having a higher solubility. In fact, apart from the vapor pressure, Henry's law constant, and octanol-water partition coefficients, NIC3 typically has the largest magnitude values for the predicted environmental properties followed by NIC1 and then NIC2 (with few exceptions). Despite its high aqueous solubility, the positive K_{oc} values suggest that DNAM may adsorb relatively strongly in soil. The K_{ow} are close to zero while K_{hept-w} is negative, which highlights DNAM's preferential solubility for water over nonpolar solvents or lipids. The predicted boiling and flash temperatures (T_{boil} and T_{flash}) illustrate DNAM's high thermal stability.

Conclusions

In this study, we investigated the effect of aqueous solvation on the nitroimine keto tautomers of DNAM through analysis of relative energies, electron affinities, ionization potentials, redox potentials, and pK_a 's using DFT (B3LYP, M06-2X functionals) and MP2 quantum chemical methods. The M06-2X results tend to fall between the B3LYP and MP2 values, and the MP2 data typically showed the least sensitivity to phase/solvation model. Our CPCM and SMD calculations predict that the three NIC conformers of DNAM are essentially isoenergetic in solution. Furthermore, in a bulk water environment DNAM's electron affinities increase and ionization potentials decrease for each NIC conformer. DNAM will be resistant to reduction. The pK_a calculations may reflect the electron-withdrawing nature of the nitroimine groups, which lends an acidic character to the triazine ring. Overall, our results suggest no major changes in reactivity with only small, modest shifts in electronic properties of DNAM in bulk water solution. Furthermore, DNAM is likely deprotonated at the N5 position at all but the most acidic pH conditions (less than 2). Further studies should include the effects of different species present in water that may influence the reactivity or degradation of DNAM when interacting with water.

Acknowledgement

The use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government. The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research conducted under the Environmental Quality Technology Program of the United States Army Corps of Engineers and the Environmental Security Technology Certification Program of the Department of Defense by the USAERDC. Permission was granted by the Chief of Engineers to publish this information. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents. This work was also supported by a grant of computer time from the DOD High Performance Computing Modernization Program at ERDC, Vicksburg. Gregory S. Tschumper acknowledges support from NSF (CHE-1664998).

Supporting Information Available

Relative electronic and Gibbs free energies of NIC1, NIC2, and NIC3; gas phase redox potentials; coordinates of optimized structures.

References

- (1) Shukla, M. K.; Boddu, V. M.; Steevens, J. A.; Damavarapu, R.; Leszczynski, J., Eds. *Energetic Materials: From Cradle to Grave*; Challenges and Advances in Computational Chemistry and Physics; Springer International Publishing: Cham, 2017; Vol. 25.
- (2) Fried, L. E.; Manaa, M. R.; Pagoria, P. F.; Simpson, R. L. Design and synthesis of energetic materials 1. *Annual Review of Materials Research* **2001**, *31*, 291–321.
- (3) Sikder, A. K.; Sikder, N. A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space applications. *Journal of Hazardous Materials* **2004**, *112*, 1–15.
- (4) Badgujar, D. M.; Talawar, M. B.; Asthana, S. N.; Mahulikar, P. P. Advances in science and technology of modern energetic materials : An overview. **2008**, *151*, 289–305.
- (5) Talawar, M. B.; Sivabalan, R.; Mukundan, T.; Muthurajan, H.; Sikder, A. K.; Gandhe, B. R.; Rao, A. S. Environmentally compatible next generation green energetic materials (GEMs). *Journal of Hazardous Materials* **2009**, *161*, 589–607.
- (6) Singh, R. P.; Gao, H.; Meshri, D. T. Nitrogen-Rich Heterocycles. **2007**, 35–36.
- (7) Gao, H.; Huang, Y.; Ye, C.; Twamley, B.; Shreeve, J. M. The synthesis of di(aminoguanidine) 5-nitroiminotetrazolate: Some diprotic or monoprotic acids as precursors of energetic salts. *Chemistry - A European Journal* **2008**, *14*, 5596–5603.
- (8) Gao, H.; Shreeve, J. M. Azole-based energetic salts. *Chemical Reviews* **2011**, *111*, 7377–7436.
- (9) Sabatini, J.; Oyler, K. Recent Advances in the Synthesis of High Explosive Materials. *Crystals* **2015**, *6*, 5.
- (10) Atkinson, E. R. The Nitration of Melamine and of Triacetylmelamine. *Journal of the American Chemical Society* **1951**, *73*, 4443–4444.

- (11) Brederick, H.; Effenberger, F.; Hajek, M. Substituierte s-Triazine : Synthese und Reaktionen von 6-Hydroxy-2,4-bis-nitramino-s-triazin. *Chemische Berichte* **1968**, *101*, 3062–3069.
- (12) Simões, P. N.; Portugal, A.; Campos, J. Characterization and kinetic analysis of the thermal decomposition of 2-oxy-4,6-dinitramine-s-triazine in non-isothermal conditions. *Thermochemica Acta* **1997**, *298*, 95–108.
- (13) Hatano, H.; Hasegawa, T.; Yoshida, T. Properties of 2-oxy-4,6-dinitramine-s-triazine (DNAM). International Pyrotechnics Seminars. Tsukuba, Japan, 1997; p 229.
- (14) Simões, P.; Pedroso, L.; Portugal, A.; Carvalheira, P.; Campos, J. New propellant component, Part I. Study of 4,6-dinitroamino-1,3,5-triazine-2(1 H)-one (DNAM). *Propellants, Explosives, Pyrotechnics* **2001**, *26*, 273–277.
- (15) Simões, P. N.; Reva, I.; Pedroso, L. M.; Fausto, R.; Portugal, A. A. Low-temperature FTIR spectroscopic and theoretical study on an energetic nitroimine: Dinitroammeline (DNAM). *Journal of Physical Chemistry A* **2008**, *112*, 3432–3443.
- (16) Hoare, J.; Duddu, R.; Damavarapu, R. A Safe Scalable Process for Synthesis of 4,6-Bis(nitroimino)-1,3,5-triazinan-2-one (DNAM). *Organic Process Research and Development* **2016**, *20*, 683–686.
- (17) Simoes, P. N.; Pedroso, L. M.; Beja, a. M. M.; Silva, M. R.; MacLean, E.; Portugal, a. a. Crystal and molecular structure of 4,6-bis(nitroimino)-1,3,5-triazinan-2-one: theoretical and X-ray studies. *The journal of physical chemistry. A* **2007**, *111*, 150–8.
- (18) Alongi, K. S.; Shields, G. C. Theoretical calculations of acid dissociation constants. A review article. *Annual Reports in Computational Chemistry* **2010**, *6*, 113–138.
- (19) Moller, C.; Plesset, M. S. Note on an Approximation. *Physical Review* **1934**, *46*, 618–622.
- (20) Head-gordon, M.; Pople, J. A. MP2 energy evaluation by direct methods. *Chemical Physics Letters* **1988**, *153*, 503–506.

- (21) Frisch, M. J.; Head-gordon, M.; Pople, J. A. Semi-direct algorithms for the MP2 energy and gradient. *Chemical Physics Letters* **1990**, *166*, 281–289.
- (22) Frisch, M. J.; Head-gordon, M.; Pople, J. A. A direct MP2 gradient method. *Chemical Physics Letters* **1990**, *166*, 275–280.
- (23) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry , thermochemical kinetics , noncovalent interactions , excited states , and transition elements : two new functionals and systematic testing of four M06-class functionals and 12 other fun. *Theoretical Chemistry Accounts* **2007**, *120*, 215–241.
- (24) Zhao, Y.; Truhlar, D. G. Density functionals with broad applicability in chemistry. *Acc Chem Res* **2008**, *41*, 157–167.
- (25) Hill, F. C.; Sviatenko, L. K.; Gorb, L.; Okovytyy, S. I.; Blaustein, G. S.; Leszczynski, J. DFT M06-2X investigation of alkaline hydrolysis of nitroaromatic compounds. *Chemosphere* **2012**, *88*, 635–643.
- (26) Sviatenko, L. K.; Kinney, C.; Gorb, L.; Hill, F. C.; Bednar, A. J.; Okovytyy, S.; Leszczynski, J. Comprehensive investigations of kinetics of alkaline hydrolysis of TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene, and DNAN (2,4-dinitroanisole). *Environ Sci Technol* **2014**, *48*, 10465–10474.
- (27) Barone, V.; Cossi, M.; Chimica, D.; Uni, V.; Ii, F.; Mezzocannone, V.; Napoli, I. Conductor Solvent Model. *Journal of Physical Chemistry A* **1998**, *5639*, 1995–2001.
- (28) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *Journal of Physical Chemistry B* **2009**, *113*, 6378–6396.

- (29) TURBOMOLE V7.2. 2017, a development of University of Karlsruhe and Forschungszentrum karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://turbomole.com>.
- (30) Klamt, A. Conductor-like screening model for real solvents: A new approach to the quantitative calculation of solvation phenomena. *J Phys Chem* **1995**, *99*, 2224–2235.
- (31) Klamt, A.; Jonas, V.; Bürger, T.; Lohrenz, J. C. Refinement and parameterization of COSMO-RS. *J Phys Chem A* **1998**, *102*, 5074–5085.
- (32) COSMOtherm, Version C3.0, Release 18.0, COSMOlogic GmbH & Co. KG, <http://www.cosmologic.de>.
- (33) Eckert, F.; Klamt, A. Fast solvent screening via quantum chemistry: COSMO-RS approach. *AIChE J* **2002**, *48*, 369–385.
- (34) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F.; Nandi, S.; Ellison, G. B. Atomic and molecular electron affinities: Photoelectron experiments and theoretical computations. *Chemical Reviews* **2002**, *102*, 231–282.
- (35) Lewis, A.; Bumpus, J. A.; Truhlar, D. G.; Cramer, C. J. Molecular modeling of environmentally important processes: Reduction potentials. *J Chem Educ* **2004**, *81*, 596–604.
- (36) Truhlar, D. G.; Cramer, C. J.; Lewis, A.; Bumpus, J. A. *J. Chem. Educ.* 2004, *81*, 596–604. *J Chem Educ* **2007**, *84*, 934.
- (37) Marenich, A. V.; Ho, J.; Coote, M. L.; Cramer, C. J.; Truhlar, D. G. Computational electrochemistry: prediction of liquid-phase reduction potentials. *Phys Chem Chem Phys* **2014**, *16*, 15068–15106.
- (38) Sviatenko, L. K.; Isayev, O.; Gorb, L.; Hill, F. C.; Leszczynska, D.; Leszczynski, J. Are the reduction and oxidation properties of nitro compounds dissolved in water different from

- those produced when adsorbed on a silica surface? A DFT M05-2X computational study. *J Comput Chem* **2015**, *36*, 1029–1035.
- (39) Sviatenko, L. K.; Gorb, L.; Hill, F. C.; Leszczynska, D.; Leszczynski, J. Structure and redox properties of 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) adsorbed on a silica surface: A DFT M05 computational study. *J Phys Chem A* **2015**, *119*, 8139–8145.
- (40) Ben-Naim, A.; Marcus, Y. Solvation thermodynamics of nonionic solutes. *J Chem Phys* **1984**, *81*, 2016–2027.
- (41) Bartmess, J. E. Thermodynamics of the Electron and Proton. *J Phys Chem* **1994**, *98*, 6420–6424.
- (42) Bartmess, J. E. Thermodynamics of the Electron and Proton [Erratum to document cited in CA121:19495]. *J Phys Chem* **1995**, *99*, 950674.
- (43) McQuarrie, D. A. *Statistical Mechanics*; University Science Books: Sausalito, CA, 2000.
- (44) Liptak, M. D.; Shields, G. C. Accurate pK_a calculations for carboxylic acids using complete basis set and Gaussian-n models combined with CPCM continuum solvation methods. *J Am Chem Soc* **2001**, *123*.
- (45) Liptak, M. D.; Gross, K. C.; Seybold, P. G.; Feldgus, S.; Shields, G. C. Absolute pK_a determinations for substituted phenols. *J Am Chem Soc* **2002**, *124*, 6421–6427.
- (46) Cooper, J. K.; Grant, C. D.; Zhang, J. Z. Ab initio calculation of ionization potential and electron affinity of six common explosive compounds. *Rep Theor Chem* **2012**, *1*, 11–19.

